

EXAMINATION OF WATER

CHEMICAL AND BACTERIOLOGICAL

BY

WILLIAM P. MASON

LATE PROFESSOR EMERITUS OF CHEMISTRY

Rensselaer Polytechnic Institute

SIXTH EDITION, REVISED

BY

ARTHUR M. BUSWELL

Professor of Chemistry, University of Illinois;

Chief, Illinois State Water Survey

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PREFACE TO THE SIXTH EDITION

WE are sure that every student who has taken a course in water analysis has felt grateful to Professor Mason for presenting the subject in so readable and entertaining a manner as he did in the former editions of *Examination of Water*.

Much of the interest and charm of this little book lay in the historical background which the author was able to furnish from his own rich experience in the field. In attempting a revision it has been our aim to preserve as far as possible the spirit of the original work. Few changes have been made except where it was necessary to bring the terminology up to date. For example, the rise of chlorination of water has made it necessary to refer to the chloride ion as "chloride" rather than as "chlorine," reserving the term "chlorine" for use when the element chlorine is referred to.

The purpose of the book has always been to supply the needs of the undergraduate student rather than those of the routine analyst. For that reason considerable space has been given to the development of a setting for the various analytical tests so that the student will see them in their true perspective.

The present edition differs from the former principally in the addition of the newer analytical procedures. The methods for the determination of *pH* and free chlorine are notable examples. A more extensive discussion of losses due to hard water and detailed direction for the systematic analysis of boiler waters also have been included. A chapter of laboratory exercises in water treatment describes procedures whereby a student may actually carry out the

common processes of water treatment, such as softening, coagulation and chlorination. The exercise on water softening is based upon a series of tests which were a part of the routine procedure used by the Kennicott Water Softening Company to determine the cost of chemicals required for treatment. This group of exercises has been found especially useful in courses designed to instruct engineering students in the principles of water examination.

The appendix has been enlarged to include certain references not easily available to the student. We are especially indebted to Dr. Hugh S. Cumming, Surgeon General of the United States Public Health Service, for permission to include Reprint No. 1029, Drinking Water Standards, to the American Railway Engineering Association for permission to include its analytical methods, and to Dr. H. E. Howe, editor of the Technologic series of the American Chemical Society monographs, and the Chemical Catalog Company, publishers, for permission to quote from monograph No. 38. To the members of the staff of the Illinois State Water Survey the writer wishes to express his appreciation for criticism and assistance.

We regret that Professor Mason's health has not made it possible for him to actively assist in this revision. His encouragement has been a stimulation to our best effort.

A. M. BUSWELL.

URBANA, ILLINOIS,
June, 1931

PREFACE TO THE FIFTH EDITION

KNOWLEDGE of quantitative analysis is here necessarily assumed; therefore the merest suggestions are given for determination of the mineral matters present in a water, while the items properly lying within the scope of a sanitary examination are dealt with more at length.

Upon the bacteriological side, only so much is touched upon as has been demonstrated to be of real service to the water examiner; leaving the great field of ultimate differentiation to be further explored, and rendered still more practically useful, by the professed bacteriologist.

Sundry tests contained in former editions have been omitted and others, more suited to modern practice, have been added in their place.

Effort has been made to place the analytical methods in harmony with the recommendations of the 1917 report of the Standard Methods Committee of the American Public Health Association, but it has been considered best not to quote directly upon too extensive a scale from that standard work, for the reason that its excellence as a book of reference interferes somewhat with its value as a working text for students' use.

RENSSELAER POLYTECHNIC INSTITUTE, TROY, N. Y.

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EXAMINATION OF WATER

CHAPTER I

INTRODUCTORY

A GREAT deal of popular misconception exists upon the subject of the analysis of potable water, and it is commonly supposed that such an examination may be looked upon from practically the same point of view as the analysis of an iron ore. That this belief is founded on fallacy may, however, be readily shown. When an iron ore is submitted for analysis the chemist determines and reports upon the percentages of iron, phosphorus, sulphur, etc., found therein; and at that point his duties usually cease, inasmuch as the ironmaster is ordinarily capable of interpreting the analysis for himself. Even should the analyst be called upon for an opinion as to the quality of the ore, the well-known properties of the several constituents make such a task an easy one, and, assuming the sample to have been fairly selected, the opinion may be written without any inquiry as to the nature of the local surroundings of the spot whence the ore was taken.

A water analysis, on the other hand, is really not an analysis at all, properly so called, but is a series of experiments undertaken with a view to assist the judgment in determining the potability of the supply. Although Standard Methods has been published, the manner of conducting these experiments is still largely influenced by the individual preferences of the analyst, and are far

from being uniform or always capable of comparison, thus often introducing elements of confusion where two or more chemists are employed to analyze the same water. Some of the substances reported—"albuminoid ammonia," for instance—do not exist ready formed in the water at all, and are but the imperfect experimental measures of the objectionable organic constituents which our present lack of knowledge prevents our estimating directly.

Thus the numerical results of a water analysis are not only unintelligible to the general public but are not always capable of interpretation by a chemist unless he be acquainted with the surroundings of the spot whence the sample was drawn and be posted as to the analytical methods employed.

It was formerly very common for water to be sent for analysis, with the request that an opinion be returned as to its suitability for potable uses, while at the same time all information as to its source was not only unfurnished but was intentionally withheld, with a view of rendering the desired report unprejudiced in character.

Such action was not only a reflection upon the moral quality of the chemist, but it seriously hampered him in his efforts to formulate an opinion from the analytical results.

For instance, a large quantity of common salt is a cause for suspicion when found in drinking water, not because of any poisonous property attaching to the salt itself, but because it is usually difficult to explain its presence in quantity except upon the supposition of the infiltration of sewage. Thus an amount of salt sufficient to condemn the water from a shallow well in the Hudson valley could be passed as unobjectionable if found in a deep-well water from near Syracuse, N. Y.

The writer once saw the contents of an ice-cream freezer dumped within a few feet of the mouth of a domestic well. So large an amount of salt thrown upon the ground naturally increased the quantity of chloride in the water, and

might have led to the condemnation of the well had not the source of the chloride been known.

Hence it is seen how important it is for the chemist to be fully acquainted with the history of the water he is to examine in order that he may compare his results in "chloride" with the "normal chloride" of the section whence the sample is taken.

A knowledge of the history of the water is no less important in order to interpret the remaining items of a water analysis. Some time since a water was sent from Florida to the author for examination and was found to contain 1.18 parts "free ammonia" per million. Much "free ammonia" commonly points to contamination from animal sources, and had it not been known that the water in question was derived from the melting of artificial ice made by the ammonia process the enormous quantity of ammonia found would have condemned it beyond a peradventure. As it was, the water was pronounced pure, the other items of the analysis having been found unobjectionable.

Analytical results which would condemn a surface water may be unobjectionable for water from an artesian well, for the reason that in the latter case high figures in "free ammonia," "chloride," or "nitrates" are often capable of an explanation other than that of sewage infiltration. Even though such a water should, at a previous period, have come in contact with objectionable organic waste material, yet the intervening length of time and great distance of underground flow would probably have furnished abundant opportunity for thorough purification.

"Deep" samples taken from the same lake, at the same spot and depth, will vary greatly in analytical results if the temperature of the water at the several dates of sampling should be markedly different, owing to the disturbing influence of vertical currents.

Again, suppose it is desired to determine whether or

not the water of a river is so contaminated with upstream sewage as to be unfit for a town supply. A single analysis of the water taken from the site of the proposed intake would very possibly be valueless. Examinations of any real value in such cases should always be of a comparative nature, and should extend over sufficient time to embrace seasonal and other changes common to such sources.

Thus it is that the chemist must be in full possession of all the facts concerning the water which he is asked to examine, in order that his opinion as to its purity may be based upon the entire breadth of his past experience, for in no branch of chemical work are experience and good judgment better exercised than in the interpretation of a water analysis.

A case such as this might arise: A water is condemned because of high chloride. It is completely sterilized by perfect filtration. After such filtration it contains as much chloride as before but is then pronounced as safely potable. Note how important it would be to possess a knowledge of the history of the water in such an instance.

However faithfully the various laboratory tests may be applied to decide the question of the fitness or unfitness of a certain water for dietetic purposes, there is nothing upon which greater stress should be laid than a thorough personal knowledge of the surroundings of the source of supply. In other words, it is essential to make a careful and thorough "sanitary survey."

It was years ago laid down as a golden rule "never to pass judgment upon a water the history of which is not thoroughly known," and the nearer this maxim is lived up to to-day the fewer will be the mistakes in the reports issued.

A water analysis is, for purposes of economy, rarely made complete. For ordinary drinking water the question is always asked, "Is it wholesome?" To answer this the analysis of the mineral residue left upon evaporation is not usually required, so that much time and expense may

be saved by simply reporting this as "total solids." On the other hand, analyses of mineral waters deal with this feature of the examination very largely, and usually to the exclusion of those portions, such as "albuminoid ammonia," "required oxygen," etc., which are important in sanitary analyses. The same may be said of the analyses of waters for boiler use. The development of bacteriological methods has changed though not lessened the usefulness of the chemical methods for the examination of water. The bacterial determinations give absolute data concerning the quality while the chemical tests give relative information.

The great advantage which the chemical tests possess is the rapidity with which they can be carried out. The whole series of chemical tests can be completed by an experienced analyst in three hours, while the bacterial tests require two to four days for completion.

The chemical tests find their greatest usefulness in the routine control of water-treatment plants. Suppose, for example the operator of a plant on the Great Lakes has established normal values for the various forms of nitrogen in the raw water. If the wind shifts to a quarter which is likely to increase the pollution at the intake, he can follow this increase by hourly chemical tests and adjust the operation of his plant accordingly.

CHAPTER II

CHEMICAL EXAMINATION OF WATER

DIRECTIONS FOR TAKING A WATER SAMPLE

ONE-GALLON glass-stoppered bottles are to be used for sampling. They should be most carefully cleaned, their stoppers covered with tin foil and tied down with cloth. Upon being taken to the field, they should be rinsed with the water to be sampled. Do not attempt to scour the interior of the neck by rubbing with either fingers or cloth. After thorough rinsing, fill the vessel to overflowing, so as to displace the air, completely empty it and then collect the sample.

One gallon of water is more than is needed for the analysis, but it is wise to have sufficient to guard against accidental losses.

If the water is to be taken from a tap, let enough run to waste to empty the local lateral before sampling; if from a pump, pump enough to empty all the pump connections; if from a stream or lake, take the sample well out from the shore, and sink the stoppered sampling vessel toward mid-depth before removing the stopper, so as to avoid both surface scum and bottom mud.

In every case fill the bottle nearly full, leaving but a small space to allow for possible expansion, and close securely. Under no circumstances place sealing wax upon the stopper, but tie the cloth firmly over the neck to hold the stopper in place. The ends of the string may be afterward sealed if necessary.

Stoneware jugs are not admissible for collecting water samples. They are hard to clean and some of the salt used for glazing may remain in the interior.

Bear in mind throughout that water analysis deals with material present in very minute quantity, and that the least carelessness in collecting the sample must vitiate the results. Note the date of taking the sample, record the temperatures of both air and water and give as full a description as possible of the soil through or over which the water flows, together with the immediate sources of possible contamination.

Sketch the surroundings of the place of collection and give approximate distances of houses, privies, barns, and fertilized land, noting the general character and topography of the local watershed; in other words, make a careful sanitary survey.

Having secured the sample, the analysis should be begun at once, for the reason that water is liable to rapid changes in character during storage. For instance, the following analyses are of the same sample of water from the laboratory tap, drawn November 10, and allowed to stand in the sampling bottle at ordinary room temperature:

TABLE 1

	Nov. 10	Nov. 12	Nov. 13	Nov. 14	Nov. 15	Dec. 15
Free ammonia.....	0.037	0.042	0.042	0.050	0.075	0.060
Albuminoid ammonia...	.220	.178	.191	.175	.155	.205
Chloride.....	4.5					
N in nitrites.....	trace	trace	trace	trace	trace	none
N in nitrates.....	.50	.525	.55	.60	.60	.60
Required oxygen.....	4.35	4.6	4.2	4.4	4.1	4.6
Total solids.....	140.					

This water shows gradual oxidation of the nitrogen contents to nitrates, but on the whole is fairly stable. As showing, on the other hand, how rapid and how irregular the storage changes may at times be, the following analyses by Liversidge are given.¹

¹ Chem. News, lxxi, 249.

These are, of course, exaggerated cases containing high ammonias, but they serve to point out the necessity of avoiding delay between the collection of the sample and the beginning of the analysis.

TABLE 2

	Horse Pond		Fish Pond		Peaty Water	
	Free ammonia	Albuminoid ammonia	Free ammonia	Albuminoid ammonia	Free ammonia	Albuminoid ammonia
December 11	10.00	7.00	0.12	0.90	0.72	0.19
12	2.00	2.00	.11	.92	1.12	.04
13	8.00	4.00	.16	1.04	1.12	.13
15	7.00	4.00	.16	1.03	1.08	.12
16	6.00	2.00	.38	.69	.03	.04
19	5.00	2.00	.52	.56	.02	.03
20	4.00	1.00	.70	.38	.01	.01
21	2.00	.50	.90	.30		
January 8	.50	.25	1.38	.06		
10	.07	.07	1.50	.04		

Determination of dissolved gases should be done in the field.

Not long since no small confusion existed on account of the many ways in which the results of water analyses were stated, but this difficulty is now nearly done away with by the more general acceptance of the recommendation that all results be given in *parts per million in weight*. This method has the advantage that a liter, or fraction thereof, of water having been operated upon, and the substances found having been determined in milligrams, no long arithmetical calculations are required.

Of course the assumption is made that a liter of water weighs a kilogram—a true enough statement for potable

waters, but one capable of introducing error when mineral waters are dealt with whose specific gravities are appreciably above unity. In such a case the water to be analyzed is actually weighed, or else its weight is estimated from the known specific gravity and volume.

It is not usual to take these precautions unless the error introduced by omitting them approaches the allowable analytical error which is ordinarily set at .2 to .3 per cent of the substance determined. Twenty-five degrees centigrade and 6500 p.p.m. are the limits for temperature and total solids, respectively. A liter of pure water at 25° C. weighs 997 grams and a liter of brine containing 6573 milligrams of NaCl weighs 1003 grams at 20° C. The neglect of temperature in the first case or concentration in the second case introduces an error of .3 per cent.

Water should not be filtered before analysis unless so specified. If sediment be present, it should be equally distributed by thorough shaking before measuring.

The reason for this is that a water analysis should represent the water as the consumer uses it, and not in a condition improved by filtration.

Water analysis cannot be conducted in a general laboratory, because many of the tests would be ruined by the fumes common to such a locality.

TURBIDITY

Turbidity was formerly reported in words, not figures. In order to express it in parts per million, the writer some years ago suggested the use of a standard suspension made by adding one gram of exceedingly fine kaolin (obtained by elutriation) to one liter of distilled water. Each cubic centimeter of this preparation will contain one milligram of suspended clay.

Whipple and Jackson improved this standard by substituting fine diatomaceous earth for the kaolin, and later the United States Geological Survey introduced the use

of Pear's precipitated fuller's earth, in which form it is used to-day. The earth is ignited, ground, passed through a 200-mesh sieve and weighed. One gram being suspended in one liter of water gives a turbidity of 1000. Suitable dilutions of this standard suspension are kept in bottles of the size used for water samples and a series of "turbidities" is thereby obtained ready for instant use. A few crystals of mercuric chloride are added to each bottle to prevent organic growths.

Such a stock solution as this, when diluted with nine times its volume of water, will permit of a platinum wire one millimeter in diameter being just visible at a depth of 100 millimeters below the water surface.

A turbidity rod, prepared for the United States Geological Survey and based upon this standard, is very convenient for use in the field.

The eye of the observer must be about 1.2 meters above the wire, and the reading should not be made in direct sunlight. The rod cannot be used for turbidities below seven. For turbidities over 500 the water should be diluted before the observation is made.²

It must be noted that high color interferes with the use of the turbidity rod. Thus the writer found that the water of the Black River at Georgetown, S. C., which showed a color of 162, gave a rod reading of 31, while its true turbidity was only five.

Any quickly subsiding material present should be classed as "sediment" rather than "turbidity." To determine this it would be best to decant the water from above such deposit and then catch it upon a weighed filter or in a Gooch crucible.

When the turbidity is very high, as it is in some rivers, it often varies markedly in settleability as well as in amount. Some operators of filter plants handling water of such a variable character have adopted the practice of determining the turbidity of the raw water both imme-

² Circular 8, Div. of Hydrography.